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Conical Intersections from Particle-Particle Random Phase and Tamm-Dancoff Approximations

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Abstract

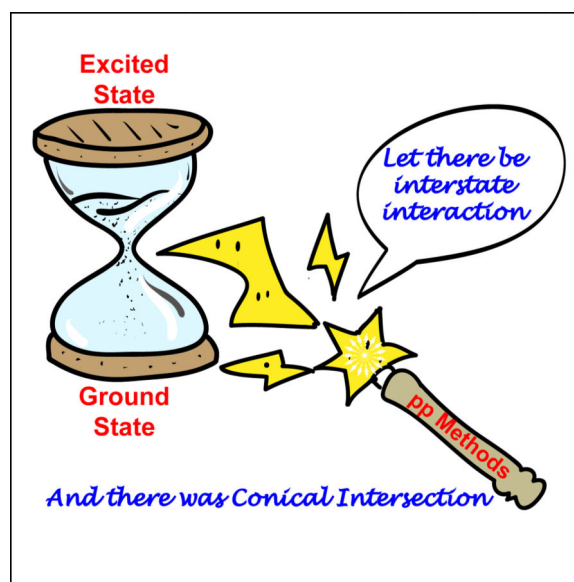
The particle-particle random phase approximation (pp-RPA) and the particle-particle Tamm-Dancoff approximation (pp-TDA) are applied to the challenging conical intersection problem. Since they describe the ground and excited states on the same footing and naturally take into account the interstate interaction, these particle-particle methods, especially the pp-TDA, can correctly predict the dimensionality of the conical intersection seam as well as describe the potential energy surface in the vicinity of conical intersections. Though the bond length of conical intersections is slightly underestimated compared with the complete-active-space self consistent field (CASSCF) theory, the efficient particle-particle methods are promising for conical intersections and non-adiabatic dynamics.

Graphical abstract

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Supporting Information Available

Summary of energetics for NH₃ at equilibrium geometry and the D_{3h} conical intersection. This material is available free of charge via the Internet at <http://pubs.acs.org/>.



The conical intersection^{1,2} is an important concept in nonadiabatic dynamics. They occur at a set of molecular geometries where two electronic states are degenerate and the potential energy surfaces intersect. Conical intersections are ubiquitous and play a vital role in many nonadiabatic processes related to energy transfer, charge transfer, and ultrafast photochemical transitions.^{2,3}

Multireference wave function methods are most frequently used to describe conical intersections. Among these methods are the complete-active-space self-consistent field (CASSCF), the complete-active-space second-order perturbation theory (CASPT2), and the multireference configuration interaction (MRCI). These methods are able to provide accurate results for conical intersections with a proper choice of the active space, however, their computational cost also quickly grows with the size of the active space, which is usually not affordable for complex systems.

Density functional theory (DFT) and linear-response time-dependent density functional theory (LR-TDDFT, or TDDFT for brevity) are widely used for ground state and excited states calculations thanks to their good balance of accuracy and efficiency.^{4,5} However, they completely fail to describe those conical intersections involving the ground state and an excited state.^{5,6} This is because the excited states, which are described by TDDFT, have no state interaction with the ground state described by DFT. Therefore, although the conical intersections should occur in a subspace of $N^{int} - 2$ dimension, with N^{int} the internal degree of freedom,² the dimension of this intersection space is incorrectly expanded by 1 with TDDFT.^{5,6}

In the past few years, many DFT-based methods have been developed to circumvent this problem by introducing the state interaction between the ground state and excited states.⁷ Li et al. directly introduced a configuration interaction coupling element to the matrix of TDDFT within the Tamm-Dancoff approximation to break the unphysical degeneracy.⁸ Van Voorhis's group developed configuration interaction based constrained density functional

theory (CDFT-CI)⁹ and well described the conical intersections with some prior knowledge on the target system.¹⁰ Based on a spin-restricted ensemble construction of the Kohn-Sham DFT (REKS) and a state-averaged (SA) energy functional, Huix-Rotllant et al. suggested a state interaction element in the SI-SA-REKS method, which also properly describes the conical intersections and yields the correct dimensionality.^{11,12} A natural introduction of the interaction is from the spin-ip (SF) TDDFT.^{13,14} It starts from a high-spin state and targets the low-spin ground and excited states by a spin-ip operator. The state interaction element between the ground and excited states are naturally built in the SF-TDDFT matrix and therefore the dimensionality of intersection space is also correct. Furthermore, the SFTDDFT has been applied to locate the geometries of conical intersections.^{12,15}

In this communication, we will apply the recently developed DFT-based particle-particle random phase approximation (pp-RPA) and particle-particle Tamm-Dancoff approximation (pp-TDA)^{16–18} to the description of conical intersections. The pp-RPA in combination with the Hartree-Fock (HF) reference has been a text-book method for describing correlation energy in nuclear physics for a long time,¹⁹ but it was not combined with DFT until very recently by van Aggelen et al.¹⁶ in electronic structure calculations. The pp-RPA and pp-TDA were also further applied to excited states calculations including both excitation energy calculation¹⁷ and geometry optimization.²⁰ These pp methods start from a two-electron deficient (N-2) reference, and target the neutral (N) states by adding two electrons, thus describing the ground and excited states on the same footing. Similar to SF-TDDFT, the interaction between ground and excited states are naturally taken into consideration. Therefore, it is expected that the pp methods can also describe conical intersections with a relatively low ($O(N^4)$) computational cost.²¹

The basic working equation for pp-RPA is

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^\dagger & \mathbf{C} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega^{\pm 2e} \begin{bmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & -\mathbf{I} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}, \quad (1)$$

with

$$A_{ab,cd} = \delta_{ac}\delta_{bd}(\varepsilon_a + \varepsilon_b) + \langle ab || cd \rangle$$

$$B_{ab,kl} = \langle ab || kl \rangle \quad (2)$$

$$C_{ij,kl} = -\delta_{ik}\delta_{jl}(\varepsilon_i + \varepsilon_j) + \langle ij || kl \rangle,$$

where a, b, c, d are virtual orbital indices and i, j, k, l are occupied orbital indices with the restrictions that $a > b, c > d, i > j$ and $k > l$. The brackets are defined as

$$\langle pq|rs\rangle \equiv \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\phi_p^*(\mathbf{r}_1)\phi_q^*(\mathbf{r}_2)\phi_r(\mathbf{r}_1)\phi_s(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (3)$$

and $\langle pq||rs\rangle \equiv \langle pq|rs\rangle - \langle pq|sr\rangle$. The eigenvectors describe the pairing matrix response to a pairing field of adding or removing electron pairs, and the corresponding eigenvalues are two-electron addition or two-electron removal energies. Starting from an N-2 reference, the energy of the neutral ground and excited states can be obtained by²⁰

$$E_0^N = E_0^{N-2} + \omega_0^{+2e}, \quad (4a)$$

$$E_n^N = E_0^{N-2} + \omega_n^{+2e}. \quad (4b)$$

where 0 and n denote the ground and excited states, respectively.

The pp-TDA is even simpler than pp-RPA. It can be obtained simply by setting the matrix \mathbf{B} in Eq. (1) to be $\mathbf{0}$ and only solving on the eigenvalue problem for matrix \mathbf{A}

$$\mathbf{A}\mathbf{X} = \omega^{+2e}\mathbf{X}. \quad (5)$$

Note here, it is known that methods with non-Hermitian Hamiltonian in principle cannot describe all conical intersections with possible complex eigenvalues.^{22,23} As a result, methods based on coupled cluster theory may face challenges for accidental same-symmetry conical intersections.^{22,23} Here before we go into the detailed performances of pp methods, we briefly comment on the Hermiticity of the pp methods. The matrices \mathbf{A} and \mathbf{C} in Eqs (1) and (5) are both Hermitian. Therefore, mathematically speaking, the pp-TDA eigenvalue problem is guaranteed to be stable with only real eigenvalues. In contrast, because of the special metric $[\mathbf{I}, \mathbf{0}; \mathbf{0}, -\mathbf{I}]$ in Eq (1), the pp-RPA in principle can have imaginary eigenvalue problems. However, till now we have never encountered this problem in regular systems thanks to the physical fact that the two-electron addition and two-electron removal processes are well decoupled. In other words, the pp-RPA solutions preserve the stability of molecules with respect to the spontaneous disproportionation reactions into two-electron addition and removal products, leading to real eigenvalues in the pp-RPA solutions. But we cannot guarantee it to also perform well for challenging accidental same-symmetry conical intersections. Therefore, although in later sections we present results both from pp-RPA and pp-TDA, we tentatively recommend pp-TDA for general conical intersection problems.

The pp calculations are performed with QM4D.²⁴ TDDFT and CASSCF calculations are performed with Gaussian09.²⁵ The B3LYP functional is used in pp-RPA and TDDFT calculations. Trihydrogen (H_3) and ammonia (NH_3) are employed as test systems. The 6-31G basis set is used for H_3 and the aug-cc-pVDZ basis set is used for NH_3 . The active space in CASSCF is chosen to be (3,6) for H_3 and (6,6) for NH_3 . To overcome the

convergence problem for regular CASSCF, SA-CASSCF is used in NH_3 , which averages over the lowest two states. Because H_3 is an open-shell doublet species, the pp methods based on unrestricted N-2 calculations generates two set of spin-contaminated data, and we average the two series to reduce the spin contamination.^{17,26}

Previously, H_3 has been used to demonstrate the problem of TDDFT as well as the success of CDFT-CI in describing conical intersections.^{6,10} For this open-shell doublet system, a seam of symmetry-required conical intersections between the lowest two doublet states is located at equilateral geometries where the singly occupied molecular orbital (SOMO) and the lowest unoccupied molecular orbital (LUMO) are degenerate. However, if we fix two atoms and only move the third one, the higher D_{3h} symmetry will reduce to lower C_{2v} or C_s symmetries and hence break the orbital and state degeneracy. Therefore, as was done in Ref. 6, we fix two atoms on the y axis with coordinates being (0, 0.409) and (0, -0.409), and place the third atom initially at (0.708, 0) with the D_{3h} symmetry and then move it along the x and y directions for scanning purpose.

The results are shown in Figure 1a–c. The reference potential energy surfaces are obtained from CASSCF(3,6)/6-31G, which is essentially a full active-space calculation within the selected basis set. The surfaces display a double-cone feature. TDDFT on top of a ground state DFT calculation provides a butterfly-like surface. The two “wings” have unphysical basins that occur at C_s symmetry. The “body” originates from the instability problem, which yields imaginary TDDFT eigenvalues that are plotted as negative ones in the figure. In contrast to TDDFT, the pp methods yield results that closely resemble the CASSCF calculations in terms of both the potential energy surface shape and the transition energy amplitude. Note that the pp-RPA reduces to the pp-TDA for this three-electron system since the dimension of **B** and **C** are both 0. The accurate double-cone surfaces indicate that the pp methods can also yield good numerical results in the vicinity of conical intersections.

NH_3 is another well studied model system.^{8,27–29} Many conical intersections can be located at planar geometries.²⁷ We first study the one with the D_{3h} symmetry. Unlike H_3 , whose D_{3h} geometries are all in the seam of conical intersections, there is only one point of degeneracy for NH_3 . At this point, the closed-shell $^1A_1'$ state and the open-shell $^1A_1''$ state are degenerate. We locate this point simply by scanning over symmetric bond stretching. Afterwards, the potential energy surfaces are scanned by extending the degree of freedom to β , which is the angle between any N-H bond and the vector that trisects the solid angle spanned by the three N-H bonds. The D_{3h} symmetry is essentially reduced to C_{3v} and the two states involved are both reduced 1A_1 when β deviates from 90° .

The results are plotted in Figure 2a–d. CASSCF, pp-RPA and pp-TDA all predict a sloped conical intersection, whereas TDDFT in combination with ground state DFT predicts a curved line of intersections due to the absence of state interaction. TDDFT also suffers from instability issues with imaginary eigenvalues when the bond length gets longer, and displays an unphysical valley because the imaginary values are plotted as negative values. For the pp methods, although their potential energy surfaces look similar to the CASSCF results, the locations of conical intersections differ from CASSCF. With the aug-cc-pVDZ basis set, CASSCF predicts a conical intersection with bond length equal to 1.487 Å, while pp-RPA

and pp-TDA predicts 1.397 Å and 1.391 Å, respectively. The bond length predicted by pp methods is smaller than that predicted by CASSCF, and in fact this is true with any given basis set. While the reason could partially lie in the fact that CASSCF lacks some dynamic correlation, it is also probable that the pp methods have some errors. It has been known that pp-RPA and pp-TDA often underestimate the equilibrium bond lengths for ground and excited states.²⁰ Therefore, it seems that the pp methods tend to underestimate the bond lengths at which chemical phenomena occur. The reason might be that the pp methods start with an N-2 SCF calculation, whose molecular orbitals are overly contracted due to the less screening of the electron-nuclei attraction compared to the neutral species. Nonetheless, it is possible that this problem may be overcome with a better choice of reference orbitals, such as using the orbitals from the neutral reference system (e.g. the HF* reference in Ref. 17).

The energy differences between the D_{3h} conical intersection geometry and the ground state geometry are also briefly investigated. The results are shown in the supporting information. It suggests that for NH₃, the pp methods perform well for the energy differences, though more general performances await further studies on more systems.

We also studied the conical intersections for NH₃ with a C_{2v} symmetry. One bond (r_1) can be freely stretched while the other two are always kept equal ($r_2 = r_3$). The bond angles are all fixed to be 120°. The contour plots in Figure 3a–c show the energy splitting between the two potential energy surfaces. The seam of conical intersections lies in between the two lines marked with 0.3 eV. Again, we can see that CASSCF and the pp methods predict similar chemical phenomena within different bond length scales. The results for pp-RPA and pp-TDA with bond length 1–1.6 Å have a roughly similar landscape as CASSCF with bond length 1–2 Å.

In summary, the pp methods can correctly describe the dimensionality of the conical intersection space. The potential energy surfaces in the vicinity of conical intersections are also well depicted. This is due to the fact that the pp methods are essentially multi-configuration approaches that describe the ground and excited states on the same footing, and naturally take into account the interstate interaction without any *ad hoc* correction elements. In this sense, it is similar to SF-TDDFT. From a quantitative perspective, the pp-RPA and pp-TDA may underestimate the bond lengths for conical intersections as a result of the contracted N-2 molecular orbitals, a shortcoming that might be overcome with different reference orbitals. Nonetheless, as an efficient DFT-based approach, the pp methods, especially the pp-TDA which in principle will never suffer from instability problems, are promising in possible applications to conical intersections and non-adiabatic dynamics.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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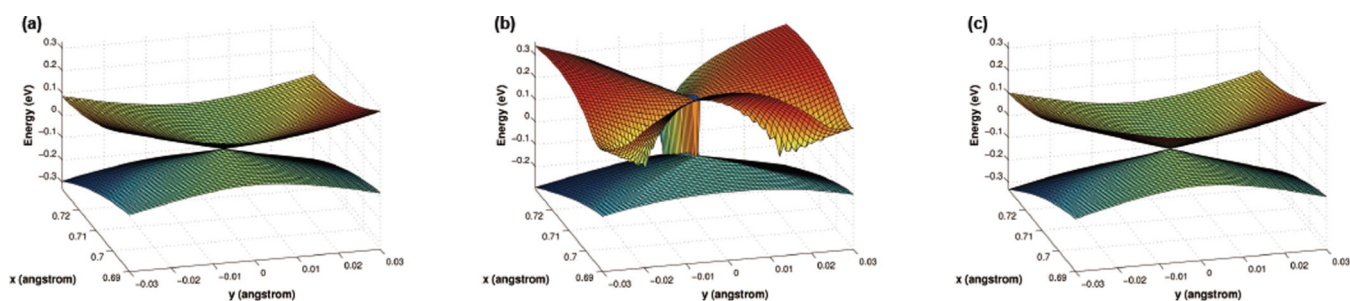


Figure 1.

Potential energy surfaces of H₃ around a conical intersection by (a) CASSCF(3,6), (b) TDDFT-B3LYP, (c) pp-RPA/TDA-B3LYP. Two atoms are fixed on the y axis at (0, 0.409) and (0, -0.409), respectively, while the position of the third atom is varied along the x and y axes. TDDFT gives an unphysical butterfly shape for the excited state surface, while the pp-RPA, which reduces to the pp-TDA in this three-electron case, correctly describes the conical intersection with potential energy surfaces closely resembling CASSCF.

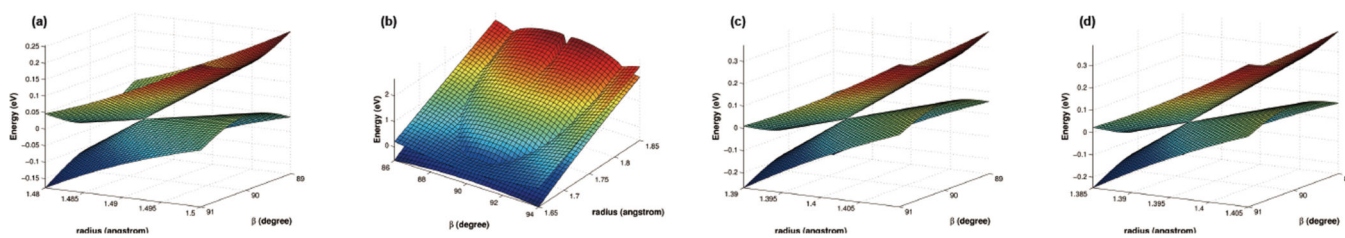


Figure 2. Potential energy surfaces of NH_3 around the conical intersection with D_{3h} symmetry by (a) CASSCF(6,6), (b) TDDFT-B3LYP, (c) pp-RPA-B3LYP, (d) pp-TDA-B3LYP. Radius denotes the bond length of the three N-H bonds, and β is the angle between any N-H bond and the vector that trisects the solid angle spanned by the three N-H bonds. TDDFT completely fails and predicts a line of intersections. In contrast, the pp methods correctly predict the double-cone feature, although the bond length of the conical intersection is shorter compared to the CASSCF result.

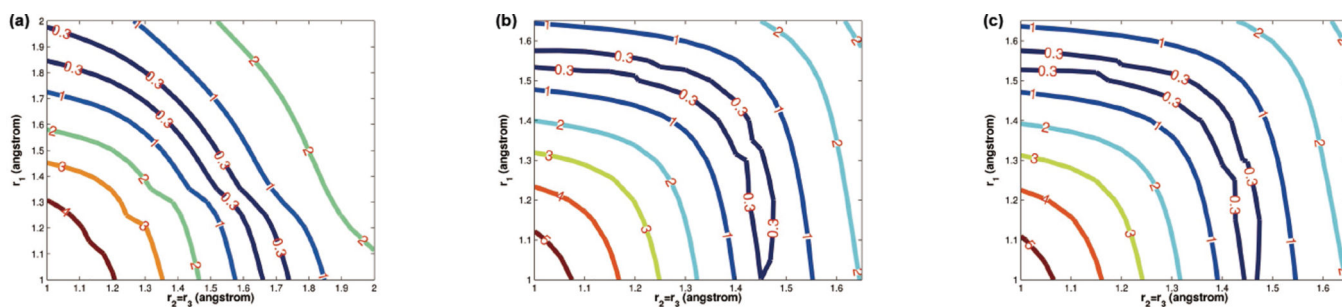


Figure 3.

Contour plot of potential energy surface splitting (in eV) near the seam of conical intersections for NH_3 with C_{2v} symmetry by (a) CASSCF(6,6), (b) pp-RPA-B3LYP, (c) pp-TDA-B3LYP. Bond angles are fixed at 120° . The plot is with respect to r_1 and $r_2(=r_3)$. The seam of conical intersections lies in between the pair of lines marked with 0.3 eV. The results from the pp methods are very similar, and with bond length 1–1.6 Å, they have a roughly similar landscape as the CASSCF results with bond length 1–2 Å.